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Interhemispheric differences in the chemical characteristics of the Indian Ocean aerosol during INDOEX

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Abstract

The water soluble inorganic part of the sub-micrometer aerosol was measured from two research vessels over the Indian Ocean during the winter monsoon season (February and March) as part of the INDOEX project in 1998 and 1999. Additional measurements were made of gas phase SO_2 from one of the vessels in 1999. All samples collected north of the ITCZ were clearly affected by continental, anthropogenic sources. A sharp transition occurred across the ITCZ with concentrations of nss-SO_4^{2-}, NH_4^+ and nss-K^+ being lower by a factor of 7–15, > 20 and > 40, respectively, on the southern side of the ITCZ. The contribution from DMS to the sub-micrometer nss-SO_4^{2-} was estimated to be up to 40% in clean air north of the ITCZ but less than 10% in polluted air originating from India. South of the ITCZ virtually all nss-SO_4^{2-} was likely to be derived from oxidation of DMS. The concentration of SO_2 decreased rapidly with distance from the Indian coast, the ratio SO_2/nss-SO_4^{2-} reaching values below 5% after 35 h travel time over the ocean. Surprisingly, MSA, which is derived from DMS, also showed higher concentrations in the sub-micrometer aerosol north of the ITCZ than south of it. This could be explained by the larger sub-micrometer surface area available north of the ITCZ for the condensation of MSA. South of the ITCZ a major part of the MSA was found on the super-micrometer particles. The total amount of MSA, on both sub-micrometer and super-micrometer particles, varied little across the ITCZ. An analysis based on the air trajectories showed that systematic variation in the observed concentrations was associated with variations in the transport from source regions. For example, differences in time since air parcels left the Arabian or Indian coasts was shown to be an important factor for explaining the substantial differences in absolute concentrations.

1. Introduction

Aerosols have been found to have a large influence on the radiative properties of the Earth's atmosphere both by the direct scattering of the incoming solar radiation (Charl-

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son et al., 1992) and indirectly by changing the properties of clouds present in the atmosphere (Twomey, 1974; IPCC, 2001). Anthropogenic activities have substantially increased the amount of aerosols present in the atmosphere and the climate effects of the anthropogenic aerosols have received large attention due the magnitude and large uncertainties of their climatic effects (IPCC, 2001). In order to reduce these uncertainties measurements of the aerosol physical and chemical properties of the aerosol are needed to trace the nature, location and strength of the sources as well as to understand their physical and chemical transformation processes occurring in the atmosphere.

The Indian Ocean during January to March is a unique location to investigate the effects of continental and anthropogenic aerosol against a background marine aerosol. Large emissions of aerosols and aerosol precursors from fossil fuel combustion (Arndt et al., 1997), biomass burning (Galanter et al., 2000) as well as soil dust (Tegen and Fung, 1994) take place over India and neighbouring countries. These aerosol particles and gases are transported with the northeasterly trade winds, mainly in the lower troposphere out over the Indian Ocean (Ramanathan et al., 1996). In addition there are large emissions of soil dust from the continental areas north and northwest of the Arabian Sea (Tegen and Fung, 1994), which are subsequently advected out over the Arabian sea. These two major airflows converge over the Indian Ocean and continue southwards. At the Inter Tropical Convergence Zone, ITCZ (usually located between the equator and 10° S at the time of the year), the polluted air will meet pristine marine air containing aerosols mainly from natural marine sources, including sea spray and dimethyl sulfide (DMS).

The Indian Ocean experiment, INDOEX, was performed over the Indian Ocean during the Asian winter monsoon season January–March. In focus was the radiative effect of the anthropogenic aerosols. The INDOEX campaign began with ship and land based observations in 1995–1997 and was intensified during a First Field Phase (FFP) during 1998 (Mitra, 1999) and culminated with the Intensive Field Phase (IFP) during 1999 which included a large variety of platforms and measurements (Ramanathan et al.,

2001). References to several detailed studies carried out as part of INDOEX are given in Sect. 3. Two of the main objectives were to asses the role of the ITCZ in the transport of aerosols and gases and to study the importance of sulfate and other continental aerosol components for the radiative forcing over the Indian Ocean (Ramanathan et al., 1996).

In this paper we present results from ship based measurements of the concentration and relative chemical composition of the water soluble inorganic fraction of the aerosol in the Marine boundary layer (MBL). The measurements were performed over the Indian Ocean during the FFP in 1998 and the IFP 1999. In addition, measurements of gas phase sulfur dioxide (SO_2) were performed during the IFP 1999. The main objectives of this study were (i) to study the role of the ITCZ in the transport of marine boundary layer aerosol and SO_2 over the Indian Ocean, (ii) to investigate the variation in concentration and relative chemical composition of the aerosol in relation to the air mass origin (iii) and to investigate the interannual difference of the aerosol between the 1998 and 1999.

2. Method

2.1. Cruise track and observing periods

The measurements were performed on board the US research vessel Ronald H. Brown during the IFP 1999 and on board the Indian research vessel Sagar Kanya during both the FFP 1998 and the IFP 1999. In total three cruises were performed, the Sagar Kanya 1998 (SK 1998) consisting of two Legs, the Sagar Kanya 1999 (SK 1999) also consisting of two Legs and the Ronald H. Brown 1999 (RB 1999) consisting of three Legs. Table 1 shows the sampling periods together with the start and end locations of each Leg. Figure 1 shows the cruise tracks for the cruises.

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2.2. Sampling

2.2.1. Particulate phase

The collection of particulate mass on board Ronald H. Brown was made from an intake located at the top of a 6 m mast in front of the bridge. The height of the collection point was 18 m above sea level.

Ambient sub-micron aerosol mass (here referred to as fpm) was determined using a filter pack set (flow rate 50 dm^{-3} min^{-1}) mounted on a sliding tray next to the entrance of the mast. The size of the sampled particles (D_{50} = 0.9 μm aerodynamic diameter, EAD) was determined by using a cyclone on the inlet (Quinn and Bates, 1989). The set held three units: two of them collected samples and one served as a sampling and an analytical blank. Each of the units consisted of one 47 mm Millipore Teflon aerosol particle filter with 1.0 μm pore size held in a polyacetal (Deldrin®) filter holder. More details are given in Leck and Persson (1996). Each sample prolonged for about 6 h.

In order to limit the sampling to periods of clean air, the pumps to the aerosol sampling systems were controlled by the ship's pollution sensor (Quinn et al., 2001). The sample air was considered to be free of ship contamination or influence from other ships in the surroundings when the relative wind speed was greater than 3 ms^{-1} and forward of the beam and with no rapid increase in number concentration of particles greater than 15 nm in diameter.

The same setup for ambient sub-micron aerosol was used on board the Sagar Kanya, but the control system for avoiding contamination was limited to wind direction.

2.2.2. Gas phase SO_2

The measurement of SO_2 was performed with an automated real-time modified Saltzman et al. (1993) technique involving high pressure liquid chromatography with fluorescence detection. The air was sampled (flow rate 6 dm^3 min^{-1}) from a heated sampling

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line with a total flow rate of 50 $dm^3\,min^{-1}$. The 0.9 μm EAD inlet used the same type of cyclone as for the fpm sampling. The inlet was placed next to the aerosol inlets and with a teflon tubing running parallel to the aerosol sampling line. To further reduce potential surface particle losses the air was drawn through a filter to remove particles. Calibration was performed with gas phase calibration using a permeation device with known emission at a specific temperature. The gas was diluted with controlled flow of zero gas to different concentrations. The detection limit was estimated to 5 pptv with accuracy of 20% and examples of calculated reproducibility were 43.2 ± 2.5 pptv (5.7%) and 21.1 ± 0.9 pptv (4.5%).

2.3. Analysis of particulate matter

All filter substrate, samples and blanks were carefully handled in a glove box (free from particles and gases such as ammonia (NH_3) and SO_2 both prior to and after collection. After exposure all filters and substrates were extracted (inside the glove box) by wetting with 0.5 cm^3 methanol and 4.5 cm^3 deionized water (Millipore Alpha-Q, resistivity 18 $M\Omega^{-1}\,cm^{-1}$). The extracts were then analyzed for major cations, major anions and methane sulfonate (CH_3SOO^-, MSA) using chemically suppressed IC. The analysis of cations used Dionex CG12A/CS12A columns and a CRSR-I auto suppressor. Strong anions were analyzed with a DIONEX AG4A/AS4A column and a CSRS-1 membrane suppressor. MSA was analyzed with a Dionex AG4/AS4 column using a stepwise elution. A Dionex ATC-1 column was used prior to the injection valve in order to retain ionic contaminants in the eluent during the run. More details are given in Quinn et al. (1998).

The average blank to sample fractions were < 5% for sulfate (SO_4^{2-}) and ammonium (NH_4^+), < 10% for nitrate (NO_3^-) and potassium (K^+), < 15% for MSA and magnesium (Mg^{2+}) and < 30% for sodium (Na^+), chloride (Cl^-) and calcium (Ca^{2+}). Duplicate samples agreed on average, within 25%.

Non-sea-salt (nss) concentrations of SO_4^{2-}, K^+ and Ca^{2+} were calculated using molar

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ratios to Na^+ or Mg^{2+} (when no Na^+ data were available) in sea water taken from Wilson (1975). All concentrations for the particulate matter and gas phase have been converted to standard atmosphere temperature and pressure (STP) by using observed temperature and pressure.

2.4. Trajectories and supporting meteorological data

2.4.1. Trajectories

Air mass back trajectories were calculated for the Ronald H. Brown cruise during IFP 1999 for the arrival height of 500 m at the ship position every six hours. The trajectories were calculated with the hybrid single-particle Langrangian integrated model HY-SPLIT 4 based on the FNL global wind field (Draxler, 1992). Trajectories for the Sagar Kanya cruises 1998 and 1999 were calculated for the arrival height of 950 hPa and at the ship position for the center time for each filterpack sample. The trajectories were calculated with the McGrath (1989) model at the European Center of Medium-range Weather Forecasts (ECMWF) using their analyzed wind and pressure fields. All trajectories were calculated for a time period of seven days backward in time.

A comparison between the two trajectory models showed that the difference was small ($<$ 500 km) for the first 100 h backwards in time and that the mean difference never exceeded 1000 km for the whole 7 days calculated period.

2.4.2. Supporting data

Meteorological parameters including surface temperature, relative humidity (RH), wind speed and wind direction (both relative and absolute), pressure and short wave radiation were measured on board both Ronald H. Brown and Sagar Kanya.

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3. Influence of the ITCZ on the Indian Ocean MBL aerosol and SO_2

One of the main objectives of the INDOEX project was to assess the role of ITCZ in the transport of trace constituents and pollutants over the Indian Ocean (Ramanathan et al., 1996). This study included four separate cross ITCZ transects: Sagar Kanya 1998 southwards during Leg 1 (SK 1998 south), Sagar Kanya 1998 northwards during Leg 2 (SK 1998 north), Sagar Kanya 1999 northwards during Leg 2 (SK 1999 north) and Ronald H. Brown 1999 northwards during Leg 1 (RB 1999 north). Figure 2 shows the cruise tracks. Also shown are the calculated trajectories for each transect and the position of the ITCZ. The concentrations of fpm for selected water-soluble components as a function of latitude relative to the ITCZ are presented in Fig. 3. The concentrations were normalized such that the median concentrations north of the ITCZ were set equal to one for each transect. Figure 3a shows that the sum of the analyzed fpm had a marked change in concentration at the position of the ITCZ. This applied to all four passages, although the median concentration ratio between north of the ITCZ and south of the ITCZ varied between 6 and 14. As seen in Figs. 3b–d a similar sharp concentration increase was observed for constituents with typical anthropogenic or continental sources like nss-SO_4^{2-} mainly from fossil fuel combustion, NH_4^+ from agriculture and nss-K^+ from biomass burning. The fpm NO_3^- was only observed in concentrations close to the detection limit and will not be further discussed. The north/south ratios for nss-SO_4^{2-}, NH_4^+ and nss-K^+ range between 6–16, 20–80 times and above 40, respectively. The relative larger concentration differences observed for nss-K^+ and NH_4^+ are consistent with their relatively weaker natural sources over the ocean (Quinn et al., 1992; Saxena, 1983) compared to that of nss-SO_4^{2-} (Ayers et al., 1996). The fpm soil dust influence, here represented by nss-Ca^{2+}, also showed slightly enhanced concentration north of the ITCZ. However, Fig. 3e shows that the variation was high and the south-north difference was not significant. No significant south-north trend was observed in the sea salt components, calculated as the sum of Na^+, Cl^-, sea salt SO_4^{2-}, sea salt K^+ and sea salt Ca^{2+}, see Fig. 3f. This suggests that the observed south

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north gradient for constituents of anthropogenic origin was not primarily caused by differences in meteorological factors, like precipitation and variability in boundary layer height. We conclude that the different origin of the air north respectively south of the ITCZ was the reason for the observed differences.

A somewhat striking result was the high concentration of fpm MSA observed in the samples collected north of the ITCZ, Fig. 4a. The coarse particulate mode (cpm) MSA was measured by Quinn et al. (2002) during RB 1999 north, Fig. 4b. The cpm MSA was found to be below detection limit north of the ITCZ. The only source of particulate MSA is the oxidation from DMS in the atmosphere (Saltzman et al., 1983). However, when comparing with the observed DMS concentrations, both in air and in sea water (only available for Ronald H. Brown cruise), no indication of higher concentrations north of the ITCZ was recorded (Bates 2002, unpublished data). Variation in the DMS concentration could therefore be ruled out as the cause of the observed gradient in the particulate MSA across the ITCZ. According to Yin et al. (1990), formaldehyde (HCHO), nitrogen dioxide, ozone (O_3) and hydrogen dioxide (HO_2) are important oxidants in the DMS oxidation scheme for the MSA production. Measurements during the RB 1999 north transect showed substantially higher concentrations of HCHO (Wagner et al., 2001) and O_3 (Stehr et al., 2002) north of the ITCZ. This would have lead to an increased production of particulate MSA in the polluted air independent of the particle size. However, the cpm MSA results during the RB 1999 north transect, Fig. 4b, was observed to be below detection limit north of the ITCZ. The sum of total analyzed MSA (fpm + cpm), Fig. 4c, shows that here was about the same concentration on both sides of the ITCZ suggesting a redistribution of MSA rather than stronger sources or sinks on either side. This indicates that the higher oxidant levels were not the major reason for the higher fpm MSA observed in the polluted air north of the ITCZ. We suggest that the available aerosol surface area might have been the cause of the observed MSA pattern. Kerminen and Leck (2001) calculated that the condensation of gas phase MSA will favor the aerosol size range with the largest available surface area. Bates et al. (2002) reported during the RB 1999 north transect significantly higher submicrometer particle

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number north of the ITCZ compared to south of the ITCZ. The calculated aerosol volume size distribution was dominated by the coarse mode in samples collected south of the ITCZ while the submicrometer aerosol dominated in the air originating from India. The aerosol surface size distribution is likely to have been even more dominated by the smaller sizes in the polluted air masses. Thus a larger fraction of gas phase MSA could then be assumed to have been condensed on the fpm north of the ITCZ. This would explain not only the higher fpm MSA observed north of the ITCZ, but also the higher cpm MSA observed in the clean air south of the ITCZ.

During the INDOEX IFP 1999 several additional measurements of aerosol and gaseous components were performed. For a direct comparison with this study one ITCZ cross transect is available (RB 1999 north). Ball et al. (2002) and Quinn et al. (2002) reported results of the fpm water-soluble ionic composition in good agreement with the present study. This is reassuring since different sampling and analytical techniques were applied. A similar south/north gradient was also found for fpm organic carbon and elemental carbon across the ITCZ (Neusüss et al., 2002). Measurements of cloud condensation nuclei during FFP 1998 (Cantrell at al., 2000) also showed a similar marked north/south gradient indicating the climatic relevance of these results.

Measurements of gases with anthropogenic origin, like carbon monoxide (CO) and O_3, also showed substantially higher concentrations north of the ITCZ on board the Ronald H. Brown during IFP 1999, as observed by Stehr et al. (2002). The difference was smaller for gases than for aerosols. In contrast to the parameters discussed above, measurements of SO_2 during the RB 1999 north, Fig. 5, did not show any south to north concentration increase. Instead a slight decrease was recorded. These noticeable results will be further discussed in Sects. 4.1 and 5.1.

All ship based particulate and gaseous measurements (SO_2 not included) were supported by aircraft measurements within the MBL (Reiner et al., 2001; Sprung et al., 2001; Wisthaler et al., 2002). The aircraft measurements showed marked differences in both gas and particulate phase constituents across the ITCZ although these differences were smaller than the ones we report here for the ship based observations

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(Sprung et al., 2001; Reiner et al., 2001). The reason might be that there was a more efficient cross ITCZ transport in the free troposphere than in the MBL, as also indicated by trajectory analysis by Verver et al. (2001). Measurements showed that major part of the pollution over the Indian Ocean was transported from southern and southeast Asia at altitudes above the MBL with a sea breeze circulation underneath it (Lelieveld et al., 2001; Reiner et al., 2001; de Reus et al., 2001; Leon et al., 2001; Welton et al., 2002). These pollution layers above the MBL might to a small extent have the potential to cross the ITCZ.

As seen in Fig. 2 the geographical position of the ITCZ varied substantially, between 14° S to 1° N, between the four cross ITCZ transects performed during this study. Figure 3 shows that there were no, or only small, cross ITCZ exchange of fpm aerosols in the MBL since the concentrations of continental fpm aerosol components were not elevated in the samples collected just south of the ITCZ. We conclude that the ITCZ should be looked upon as an effective barrier for transport of MBL fpm aerosols during the winter monsoon season over the Indian Ocean. Irrespective of the latitudinal position of the ITCZ, the air north of the ITCZ was influenced by anthropogenic and continental sources whereas the air south of the ITCZ showed no such influence.

In the following sections an effort is made to seek causes for the observed variations in the particulate absolute concentration north respective south of the ITCZ. The analysis will be based on the data set that was collected during the Ronald H. Brown 1999 cruise, since this cruise contains the largest number of samples.

4. Variations in the Indian Ocean MBL aerosol north of the ITCZ

The RB 1999 samples were classified into different groups according to the appearance of the trajectories. This classification was made independent of the position and date of sampling. Five major groups were identified.

– *Clean air south of the ITCZ (cleanS)*: Trajectories with origin in the southern Indian Ocean with no contact with land. The prevailing arrival direction at the ships were

from the south, Fig. 6a. This data set is described in Sect. 5.

- *Clean air north of the ITCZ (cleanN)*: Trajectories with origin in the northern Indian Ocean but with no indication of contact with land during the last seven days. The prevailing arrival direction at the ships was from the north, Fig. 6b.
- *Arabian sea (Arab)*: Trajectories from the Arabian Sea and the surrounding land areas but with no Indian subcontinent contact. Fig. 6c.
- *Small Indian influence (sInd)*: Trajectories that originated, or passed over, densely populated or industrialized places in the Indian subcontinent with more than 5 days of transport time since last contact with India, or trajectories that only passed a short distance over the Indian subcontinent. Fig. 6d.
- *Large Indian influence (lInd)*: Trajectories that originated, or passed over, densely populated or industrialized areas in the Indian subcontinent with less than 5 days of transport time since last contact with India or samples with less than 2 days of transport time since last contact with India. Fig. 6e.

Statistics on absolute concentration for the different trajectory groups are shown in Table 2.

4.1. Anthropogenic components

Samples with trajectories originating over India, (sInd and lInd) showed the highest concentrations of the anthropogenically derived constituents, nss-SO_4^{2-}, NH_4^+, nss-K^+, as well as for the sum of total analyzed fpm mass with nss-SO_4^{2-} and NH_4^+ as the major components. Overall, the concentrations in the sInd group were about half of those in the lInd group. Our results were consistent with source estimations for biomass burning (Galanter et al., 2000), SO_2 (Arndt et al., 1997) and NH_4^+ (Bouwman et al., 1997) which indicate large sources in India.

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Among the samples collected north of the ITCZ, the samples representing the cleanN group showed the lowest concentrations of anthropogenic constituents, as well as the lowest median total sum.

The observed variation in the anthropogenic constituents within the lInd, sInd and cleanN groups was related to the time since last contact with India (T_{Ind}) or with any continental area (T_{land}), cf. Table 2. The highest concentrations were associated with a median T_{Ind} = 52 h (lInd) and the lowest with a median T_{land} > 170 h (cleanN). We attribute the difference to increasing influence of deposition losses with increasing time of transport over the Indian Ocean.

The lack of south to north SO_2 gradient (Fig. 5), may seem surprising in view of the strong Indian sources of SO_2 (Arndt et al., 1997). However, when sorting the SO_2 data according to trajectory groups a consistent pattern evolved, Table 2, with the most polluted cases (lInd) showing the highest median SO_2 concentrations. Figure 7a shows that the SO_2 concentration decreased substantially well before T_{Ind} equals to 60 h. By comparing the SO_2 concentration with the nss-SO_4^{2-} levels, Figure 7b, a more rapid decrease was observed for SO_2 than for nss-SO_4^{2-}. The larger loss for SO_2 relative to nss-SO_4^{2-} was probably due to its higher dry deposition rate together with gas to particulate phase oxidation (Langner and Rodhe, 1991). Over the Indian Ocean, as shown in Fig. 7b and Table 2, the levels of SO_2 were at the most 10% of the recorded fpm nss-SO_4^{2-} concentrations. The observed variability in fpm nss-SO_4^{2-} over the Indian Ocean north of the ITCZ could therefore not be explained by the observed levels of SO_2.

4.2. Soil dust

The samples with trajectories originating from the Arabian Sea or from the surrounding land areas, Arab, had similar absolute fpm sum as the sInd group. However the former were more enriched by nss-Ca^{2+}. The estimated large source area for dust (Tegen and Fung, 1994) in the land areas around the Arabian sea caused the relatively elevated

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concentrations of nss-Ca^{2+} compared to the other aerosol constituents. The Ca^{2+}/Na^{+} molar ratio can be used to indicate the influence of continental sources relative to sea salt sources. The observed median Ca^{2+}/Na^{+} molar ratio in the Arab was higher (0.34) than in the sInd (0.26), indicating a larger soil dust influence in the Arab group. On the other hand, the results relative to the IInd group showed opposite values with both nss-Ca^{2+} levels and Ca^{2+}/Na^{+} ratio exceeding those of the Arab group. This is likely to be due to the more limited time since last contact with India (median $T_{\mathrm{Ind}} = 52\,\mathrm{h}$) compared to the time since last contact with land around the Arabian sea (median $T_{\mathrm{Arab}} = 120\,\mathrm{h}$) and hence larger influence by deposition in the latter group.

4.3. Sea salt

Studies in clean marine areas have observed the logarithm of the sea salt concentrations in the atmosphere (both number and mass) to be in linear relation to the local wind speed due to wave action on the sea surface (O'Dowd et al., 1997; Quinn et al., 2000; Nilsson et al., 2001; Leck et al., 2002a). However, a MBL affected by anthropogenic or continental sources has been reported to contain a modified sea salt distribution. Elevated concentrations of Cl^{-} and Na^{+} have been found in particulate and precipitation samples from the Indian continent (Kulshrestha et al., 1995; Norman et al., 2001) indicating other potential sources than the ocean, probably soil dust. This is consistent with this study, showing that the fpm Na^{+} concentrations were slightly elevated in the samples with short time since last contact with land (Arab and IInd), cf. Table 2. The lack of significant covariation ($r^2 < 0.2$) between local wind speed and logarithm of the sea salt concentration in the samples points in the same direction.

The acidity of the particles also affects the sea salt distribution by a loss of Cl^{-} increasing towards low pH. The Cl^{-}/Na^{+} molar ratio of sea salt particles has been observed to decrease with increasing particle acidity from the molar ratio of pure seawater sodium chloride (NaCl) of 1.17 (Keene et al., 1998). To investigate the importance of an increased acidity for the Cl^{-} depletion, we used the calculated difference between

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the sum of equivalent concentration of analyzed anions and cations as an indication for level of "acidity" in the samples. As shown in Fig. 8, an increasing "acidity" resulted in more depletion of chloride, with molar ratios below 0.2 for samples with highest "acidity". Also the median ratio for the different trajectory groups varied in this way with Cl^-/Na^+ molar ratios of around 0.6 in the cleanN group and then decreasing to 0.13 in the sInd and to 0.06 in the IInd. This in line with the increasing level of pollution.

We conclude the variation in the sea salt components north of the ITCZ to be related mainly to the depletion of Cl^-, with some indication of additional contribution from continental sources.

5. Variations in the Indian Ocean MBL aerosol and SO_2 south of the ITCZ

The discussion below is separated according to contribution from the two major sources, biogenic sulfur and sea salt.

5.1. DMS derived components

The observed fpm MSA/nss-SO_4^{2-} molar ratio was on average around 3%. This is in agreement with other measurements performed in unpolluted air over tropical waters (Bates at al., 1992; Bates et al., 2001; Leck et al., 2002b), and also in line with values from model calculations (Ayers et al., 1996) at similar temperatures and latitudes as this study. This suggests that the observed fpm nss-SO_4^{2-} originated from the oxidation of DMS, supporting the conclusion in Sect. 3 that there was no, or only marginal, influence of continental or anthropogenic sulfur sources south of the ITCZ.

A major fraction (~75%) of the total particulate MSA was associated with the cpm (comparison with data from Quinn et al., 2002). As discussed in Sect. 3, the condensation of MSA seemed to have favored the largest available aerosol surface. Measurements being representative of clean air during INDOEX IFP south of ITCZ by Bates et al. (2002) showed the aerosol surface to be larger in the cpm than in the fpm, which is

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consistent with the enhanced cpm MSA values.

We concluded that the observed variation in SO_2, nss-SO_4^{2-} and MSA concentrations was related to variations in the DMS source or to some extent variation in the oxidant concentrations.

Assuming the nss-SO_4^{2-} south of ITCZ to be representative for biogenic SO_4^{2-} sources over the Indian Ocean, the contribution north of the ITCZ from biogenic sources of the total fpm nss-SO_4^{2-} could be calculated. This calculation indicated that up to 40% of the nss-SO_4^{2-} in the cleanN group, < 20% in Arab and sInd groups, while only a small fraction (< 10%) in the most polluted cases (lInd group) originated from biogenic sulfur. The same comparison for SO_2 showed that a major fraction of the SO_2 over the Indian Ocean north of the ITCZ originated form a biogenic source. The only exception was for samples with T_{Ind} less than 60 h.

The observed variation in NH_4^+ was larger than for nss-SO_4^{2-} causing the observed variation in the NH_4^+/nss-SO_4^{2-} molar ratio (Table 2). The median fpm NH_4^+/nss-SO_4^{2-} molar ratio was 0.3 (Table 2) substantially lower than the value around 1 typically reported elsewhere (Covert et al., 1988; Leck and Persson, 1996). Measurements by Huebert et al. (1996) showed a decreasing NH_4^+/nss-SO_4^{2-} molar ratio with increasing particle size. The volume size distribution observed simultaneously with our measurements by Bates et al. (2002) showed the submicrometer volume to be shifted towards 1 μm diameter, suggesting a low molar ratio. However, the observed values were still lower than those reported by Huebert et al. indicating either a lack of available NH_3(g) or a chemical composition of the preexisting particles that prevented NH_3(g) uptake.

5.2. Sea salt

In samples that were not influenced by continental sources the sea salt varied according the local wind speed.

$$\log_{10}[\text{sea salt}, \mu\text{g m}^{-3}] = 0.049 * |U, \text{ms}^{-1}| - 1.3 \quad (1)$$

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The local wind speed could explain a major part of the variation in the fpm sea salt (r^2 = 0.6). The absence of anthropogenic influence (SO_4^{2-}) also strongly reduced the particle acidity (as calculated in Sect. 4.1) compared to north of the ITCZ. The median fpm Cl^-/Na^+ molar ratio was 1.0, showing only small depletion of Cl^- and thus concluded not be of significance for the observed variability in Cl^- and sea salt.

These results indicate that, in contrast to north of the ITCZ, the sea salt concentration south of the ITCZ was dependent on the local wind speed. Some of the fpm variation could also be attributed to the integrated wind speed along the air trajectory one week backward in time.

6. Interannual variation in the Indian Ocean MBL submicrometer aerosol

The measurements of fpm during both INDOEX FFP 1998 and IFP 1999 gave us a unique possibility to compare not only the variation between 1998 and 1998 but also two separate efforts during 1999 (spatial and temporal variation).

The relative chemical composition collected during RB 1999 north of the ITCZ (Fig. 9a and Table 2) was remarkable constant despite the differences in absolute concentration, as discussed in Sect. 4. The relative chemical composition was dominated by NH_4^+ and nss-SO_4^{2-}. The contributions from nss-K^+ and the sum of the sea salt components were small with the remaining components negligible. The relative chemical composition during the RB 1999 agreed with that from the Sagar Kanya cruises (1998 and 1999) within 10% for the major components. In general, the relative chemical composition south of the ITCZ showed larger variation than north of the ITCZ during all cruises (shown for RB 1999 in Fig. 9b and Table 2). The relative chemical composition south of the ITCZ was dominated by nss-SO_4^{2-} with the sum of the sea salt components and NH_4^+ as other major components.

A comparison of absolute concentrations during all three cruises, divided into the trajectory groups cleanS, Arab, sInd and lInd, is shown in Fig. 10. The variation between the trajectory groups for the Sagar Kanya cruises exhibited the same general

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pattern as for the RB 1999 data set. This support that the same processes causing the variation in concentration and chemical composition within the RB 1999 data set, as presented in Sects. 4 and 5, also applied for both the SK 1998 and the SK 1999 data sets.

However, there were several distinct differences in the absolute concentrations between the data sets were observed. In general, higher concentrations of all constituents occurred during RB 1999, in all trajectory groups, than during SK 1998. For some constituents (total sum, NH_4^+ and sea salt) this also applied for SK 1999 in comparison to SK 1998. However, large differences in absolute concentrations were also observed between the RB 1999 and SK 1999 cruises. In order to seek causes for the interannual variation as well as the variation between the two 1999 cruises, we investigated the variation in source and sink strength, the location of the source area and time the air spent over the Indian Ocean since last contact with the Arabian and Indian coast.

The absolute concentrations of the anthropogenic and continental constituents were observed to be substantially higher (2–4 times) in the lInd and sInd groups during the RB 1999 cruise compared to the SK 1998. In the case of lInd, the median time of transport since last contact with India was found to be longer (T_{Ind} = 110 h) during the SK 1998 cruise compared to the 1999 cruises (T_{Ind} = 50 and 60 h for RB 1999 and SK 1999, respectively). The shorter transport times in 1999 were associated with strong northeasterly flow over the Indian continent in February and March 1999 (Verver et al., 2001; Rasch et al., 2001). The potentially larger deposition losses in 1998 are likely to have contributed to the lower concentrations during the SK 1998 cruise.

For the sInd group there was no such correlation with the T_{Ind}. However, by comparing the origin of the trajectories, a difference in source region was identified. During the SK 1998 cruise a major part of the trajectories in the sInd group passed Sri Lanka with no contact with the Indian subcontinent during the last 7 days. This was not the case for the 1999 cruises. The sources of the anthropogenic components (Arndt et al. 1997; Bouwman et al., 1997), are estimated to be smaller in Sri Lanka than in India. This variation in source region could possibly explain the lower concentrations observed also

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in the sInd group during 1998. The difference in concentrations of the anthropogenic constituents between RB 1999 and SK 99 could not be attributed to similar differences in transport and remains to be explained.

The concentration of soil dust (nss-Ca^{2+}) was found to be more than twice as high in the Arab samples during the RB 1999 cruise than during the SK 1999 and SK 1998 cruises. The RB 1999 Arab samples were collected during March 1999 and during that month unusually strong outflow from the dry areas around the northern Arabian Sea was observed (Verver et al., 2001). Model studies of the soil dust over the Arabian Sea by Rasch et al. (2001) also showed elevated concentrations during March 1999 in contrast to both February 1999 (mainly the sampling period for Arab during SK 1999) and March 1998 (sampling period for SK 1998). This could thus possibly explain the higher nss-Ca^{2+} concentrations in the Arab group during RB 1999.

The sea salt concentration was elevated in 1999 compared to 1998. The study by Verver et al. (2001) indicated stronger winds over the Indian Ocean during January–March in 1999 than in 1998, possibly contributing to the higher concentrations. The concentration of fpm constituents with biogenic origin was, on average, 2–8 times higher during RB 1999 than during SK 1998 and SK 1999. We suggest that variations in source strength and source area could explain this variation, but due to limited amount of data this could not be verified.

Although the data showed some differences, both between 1998 and 1999 and in-between the two 1999 cruises, which we were not able to explain, we believe that the conclusions in Sects. 4 and 5 are representative for each data set. We conclude that variations in source strength, source area and time of transport over the Indian Ocean were important causes for variations in concentration. However these factors could not explain all interannual and spatial variations.

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7. Conclusions

The water soluble inorganic part of the sub-micrometer aerosol was measured from two research vessels over the Indian Ocean during the winter monsoon season (February to March) within the frames of the INDOEX project during 1998 and 1999. Additional measurements of the gas phase SO_2 were performed from one research vessel during the INDOEX IFP 1999.

One of the main goals of this study was to investigate the role of the ITCZ for the transport of MBL aerosol and SO_2. We found the ITCZ to be an effective barrier for sub-micrometer particles in the MBL with no indication of transport across the ITCZ. Irrespective of the latitudinal position of the ITCZ all samples collected north of the ITCZ were found to be influenced by anthropogenic and continental sources with 6–16, 20–80 and > 40 times higher concentrations than south of the ITCZ for nss-SO_4^{2-}, NH_4^+ and nss-K^+, respectively. There was no, or only marginal, influence of continental or anthropogenic nss-SO_4^{2-} south of the ITCZ and the variation in concentration was attributed to variation in the marine biogenic sources. The contribution from marine biogenic sources to the fpm nss-SO_4^{2-} north of the ITCZ was estimated to be up to 40% in clean air but less than 10% in polluted air originating from India.

MSA showed surprisingly a similar variation with higher absolute fpm concentration in the polluted air north of the ITCZ as the anthropogenic constituents. South of the ITCZ ~75% of the total MSA was associated with the cpm aerosol, while north of the ITCZ the MSA almost completely was found on the fpm particles. The distribution of the aerosol surface area available for the condensation of gaseous MSA into particulate phase was suggested to be the reason for this variation.

The observed concentrations of SO_2 showed a lack of south to north gradient across the ITCZ. Only samples with time since last contact with India less than 60 h showed a noticeable anthropogenic influence. The SO_2 concentrations made up for at the most 10% of the observed sub-micrometer nss-SO_4^{2-} north of the ITCZ. We conclude that the observed variation in fpm nss-SO_4^{2-} over the Indian Ocean could not be explained

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by the locally observed levels of SO_2.

The sea salt concentration in aerosols south of the ITCZ was found to be somewhat dependent on the local wind speed. However, north of the ITZC the variation was mainly related to the depletion of chloride in correlation with calculated particle acidity, but also with some indication of contribution from continental sources.

The variation in total analyzed sub micrometer concentrations north of the ITCZ was interpreted in terms of variations in source region, source strength and time of transport over the Indian Ocean. One of the main reasons for the observed differences in anthropogenic constituents, seemed to be the variation in deposition losses due to different time of transport over the Indian Ocean. The highest concentrations were associated with the shortest time since last contact with India.

The soil dust concentration was enriched in samples with trajectories originating over land areas around the Arabian Sea. Highest concentrations were observed in March 1999 during a period with observed unusual strong outflow from land areas north of the Arabian Sea.

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Table 1. Sampling periods and start and stop positions for the three cruises included in this study. Coordinates are Male, Maldives, 4.1° N, 73.3° E; Port Louise, Mauritius, 20.2° S, 57.5° E; Panjim, India, 15.7° N, 73.9° E; Goa, India, 18.2° N, 73.4°

		Start date	Start position	stop date	stop position
Sagar Kanya 1998	Leg 1	1 Mar., DOY 60	Male	12 Mar., DOY 71	Port Louise
(SK 1998)	Leg 2	15 Mar., DOY 74	Port Louise	30 Mar., DOY 89	Goa
Sagar Kanya 1999	Leg 1	21 Jan., DOY 21	Panjim	10 Feb., DOY 41	Port Louise
(SK 1999)	Leg 2	18 Feb., DOY 49	Port Louise	10 Mar., DOY 69	Panjim
Ronald H Brown 1999	Leg 1	22 Feb., DOY 53	Port Louise	28 Feb., DOY 59	Male
(RB 1999)	Leg 2	4 Mar., DOY 63	Male	23 Mar., DOY 82	Male
	Leg 3	26 Mar., DOY 85	Male	30 Mar., DOY 89	Male

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Table 2. The fpm 25, 50 and 75 percentile concentrations and molar ratios for the different trajectory groups from the Ronald H. Brown cruise in 1999. The time since last contact with land refers to any land (T_{land}) for cleanN, cleanS and North ITCZ, to India (T_{Ind}) for sInd and lInd and to other land than India (T_{Arab}) for Arab. Sea salt was calculated as the sum of Na^+, Cl^-, sea salt Mg^{2+}, sea salt K^+, sea salt SO_4^{2-} and sea salt Ca^{2+}

		MSA nmol m^{-3}	Cl^- nmol m^{-3}	NO_3^- nmol m^{-3}	NA^+ nmol m^{-3}	NH_4^+ nmol m^{-3}	Mg^{2+} nmol m^{-3}	nss-SO_4^{2-} nmol m^{-3}	nss-Ca^{2+} nmol m^{-3}	nss-K^+ nmol m^{-3}
cleanS	25 prc	0.07	0.68	<DL	1.2	0.4	0.05	2.3	0.15	<DL
	50 prc	0.09	1.2	<DL	1.3	1.1	0.17	4.1	0.33	0.04
	75 prc	0.12	2.5	0.08	2.5	2.3	0.43	4.8	0.87	0.08
North	25 prc	0.14	<DL	0.07	0.9	22.6	0.10	12.9	0.19	1.4
ITCZ	50 prc	0.21	0.25	0.27	1.6	35.6	0.26	23.6	0.50	3.7
	75 prc	0.26	0.52	0.47	2.3	53.0	0.37	39.5	0.88	6.5
cleanN	25 prc	0.14	0.24	<DL	0.5	6.8	0.07	6.1	0.08	0.48
	50 prc	0.21	0.60	0.09	1.1	22.6	0.10	11.5	0.15	1.4
	75 prc	0.26	1.1	0.19	1.7	32.7	0.19	16.5	0.20	3.1
Arab	25 prc	0.13	<DL	0.19	1.1	23.5	0.17	13.1	0.39	1.2
	50 prc	0.18	0.3	0.41	1.8	35.5	0.35	23.6	0.63	3.2
	75 prc	0.23	0.5	0.61	2.6	48.2	0.44	30.9	1.0	4.3
sInd	25 prc	0.14	0.01	<DL	0.8	20.0	<DL	13.6	0.25	2.0
	50 prc	0.22	0.18	0.10	1.6	34.7	0.18	22.6	0.32	4.3
	75 prc	0.27	0.41	0.30	2.0	52.6	0.27	40.9	0.40	6.5
lInd	25 prc	0.20	<DL	0.14	1.4	49.6	0.22	34.4	0.63	4.8
	50 prc	0.21	0.13	0.37	1.9	69.1	0.29	54.9	0.97	8.3
	75 prc	0.25	0.55	0.48	2.2	92.6	0.30	60.8	1.1	9.3

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Table 2. continued

	Sea salt $\mu g\ m^{-3}$	Sum $\mu g\ m^{-3}$	Cl^-/Na^+ molar ratio	MSA/nss-SO_4^{-2} molar ratio	NH_4^+/nss-SO_4^{-2} molar ratio	Ca^{2+}/Na^+ molar ratio	SO_2/SO_4^{2-} molar ratio	SO_2 nmol m^{-3}	Number of samples	Time since last contact with land (h)
cleanS	0.060	0.4	0.67	0.023	0.2	0.11	0.36	1.3	14	>170
	0.081	0.5	0.97	0.029	0.3	0.12	0.44	1.6		>170
	0.162	0.6	1.03	0.034	0.5	0.59	0.56	2.1		>170
North	0.036	1.7	0.00	0.006	1.3	0.22	0.02	0.7	92	76
ITCZ	0.059	3.2	0.13	0.008	1.4	0.34	0.05	1.1		120
	0.085	5.0	0.33	0.012	1.7	0.51	0.08	1.5		>170
cleanN	0.030	1.0	0.40	0.012	1.1	0.08	0.05	0.7	18	>170
	0.054	1.6	0.58	0.019	1.5	0.16	0.10	0.9		>170
	0.094	2.3	0.77	0.028	2.0	0.25	0.33	1.5		>170
Arab	0.033	1.9	<DL	0.006	1.4	0.27	0.02	0.7	43	87
	0.065	3.1	0.13	0.008	1.5	0.34	0.05	1.1		120
	0.095	4.1	0.23	0.009	2.3	0.53	0.08	1.4		>170
sInd	0.035	1.8	0.04	0.006	1.1	0.20	0.03	0.5	18	72
	0.053	3.0	0.13	0.008	1.3	0.26	0.04	0.6		165
	0.069	5.4	0.35	0.012	1.5	0.42	0.08	1.0		>170
lInd	0.049	4.5	<DL	0.003	1.1	0.37	0.02	1.1	13	35
	0.056	7.6	0.06	0.004	1.5	0.49	0.02	1.5		52
	0.067	8.0	0.14	0.007	1.6	0.58	0.05	2.2		92

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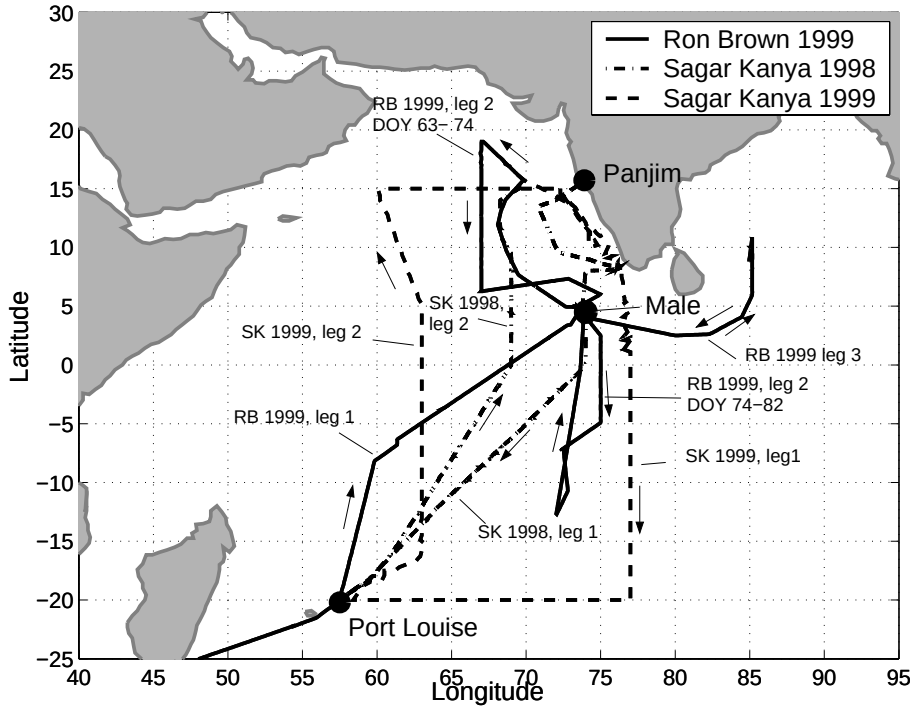

Fig. 1. Cruise tracks for the Ronald H. Brown 1999 cruise and the Sagar Kanya 1998 and 1999 cruises. The arrows along the cruise tracks show the traveling direction of the ship.

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Interhemispheric differences during INDOEX

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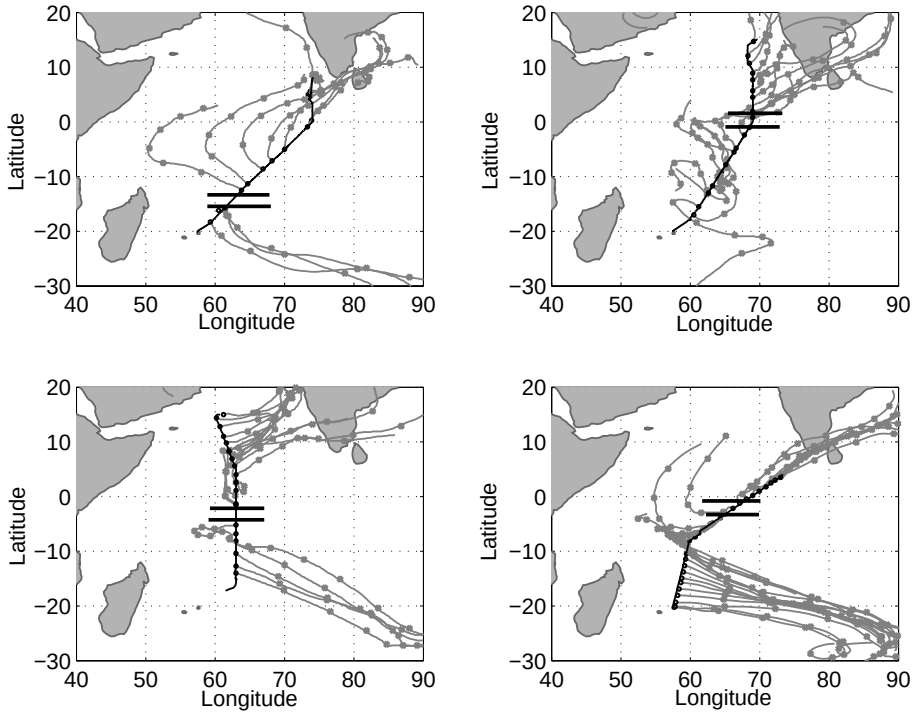

Fig. 2. Cruise tracks and trajectories during the four ITCZ passages. **(a)** Sagar Kanya 1998 southwards during Leg 1 (SK 1998 south), **(b)** Sagar Kanya 1998 northwards during Leg 2 (SK 1998 north), **(c)** Sagar Kanya 1999 northwards during Leg 2 (SK 1999 north), **(d)** Ronald H. Brown 1999 northwards during Leg 1 (RB 1999 north). The ITCZ was identified both by trajectories and meteorological observations on board the ships and the ITCZ is marked with double solid lines in each figure.

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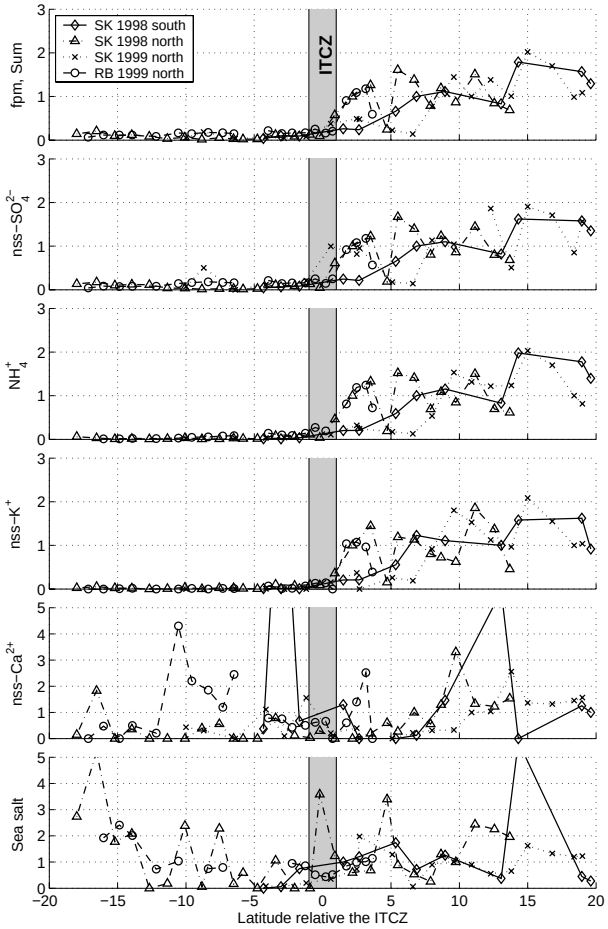

Fig. 3. The concentration of the fpm aerosol during the cross ITCZ passages as a function of latitude relative to the ITCZ. The concentrations are normalized to the median concentration north of the ITCZ for each passage. SK = Sagar Kanya and RB = Ronald H. Brown.

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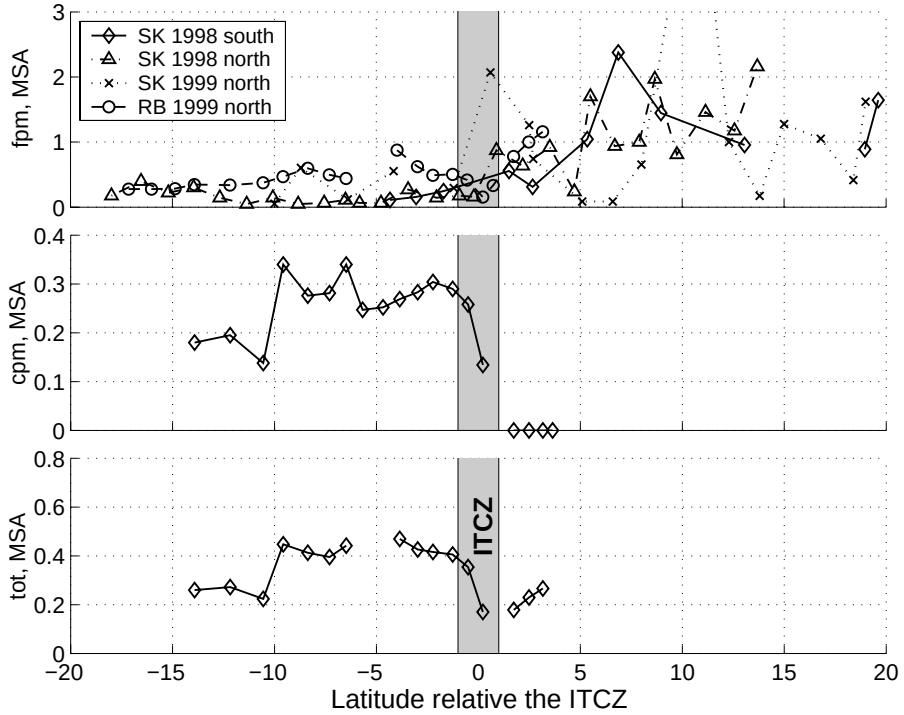

Fig. 4. (a) The concentration of MSA during the four cross ITCZ passage. The concentrations are normalized to the median concentration north of the ITCZ. **(b)** cpm MSA during the cross ITCZ passage from Ronald. H. Brown in 1999 in nmol m^{-3}. **(c)** Total MSA (fpm + cpm) during the cross ITCZ passage from Ronald. H. Brown in 1999 in nmol m^{-3}. The latitude is given as a function of latitude relative to the ITCZ.

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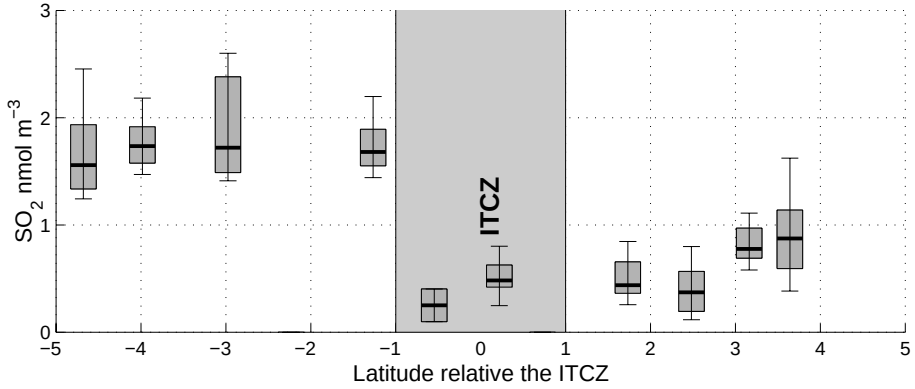

Fig. 5. The SO_2 concentration across the ITCZ during the RB 1999 north as medians over the aerosol sampling time (~6 h). The box includes data between the 25 and 75 percentiles and the vertical bars represent the 10 and 90 percentiles.

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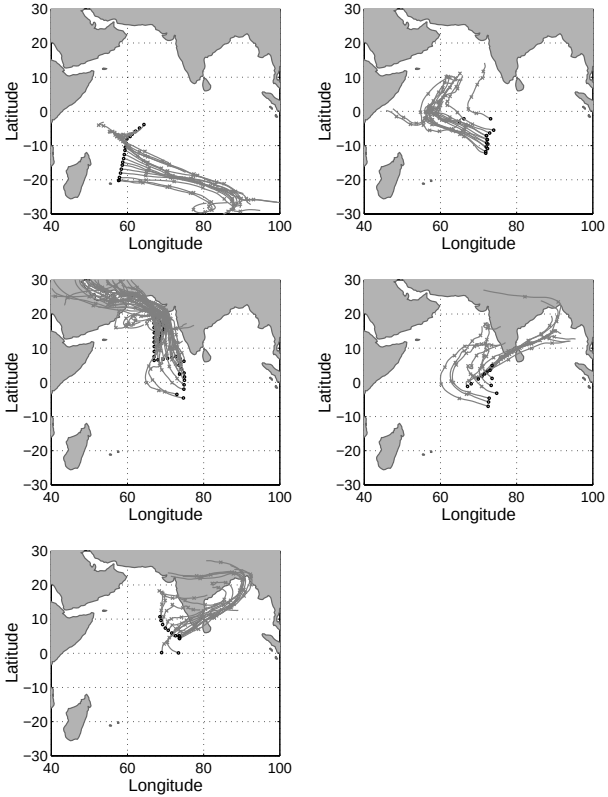

Fig. 6. Trajectories for the Ronald H. Brown 1999 cruise, sorted into different groups according to origin of the air. **(a)** South of the ITCZ (cleanS), **(b)** north of the ITCZ with no indication of contact with land (cleanN), **(c)** Arabian sea or surrounding land areas (Arab), **(d)** small Indian influence (sInd), **(e)** large Indian influence (lInd).

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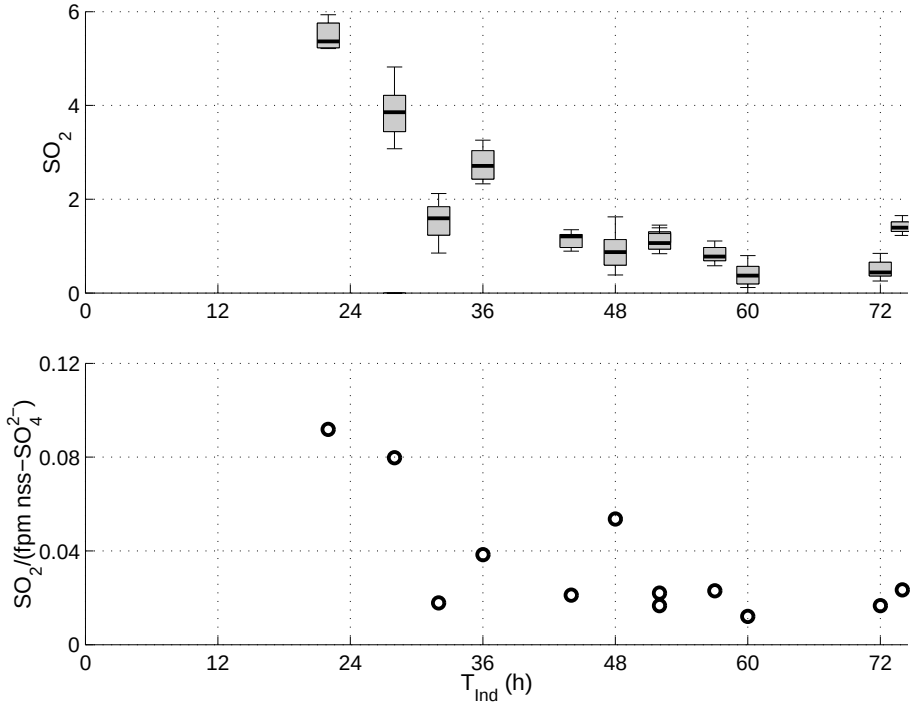

Fig. 7. **(a)** The SO_2 concentration as medians over the aerosol sampling time (~6 h) as a function of transport time from India during the Ronald H. Brown cruise in 1999. The box includes data between the 25 and 75 percentiles and the vertical bars represent the 10 and 90 percentiles. **(b)** The SO_2/(fpm nss-SO_4^{2-}) molar ratio, as a function of transport time from India during the Ronald H. Brown cruise in 1999.

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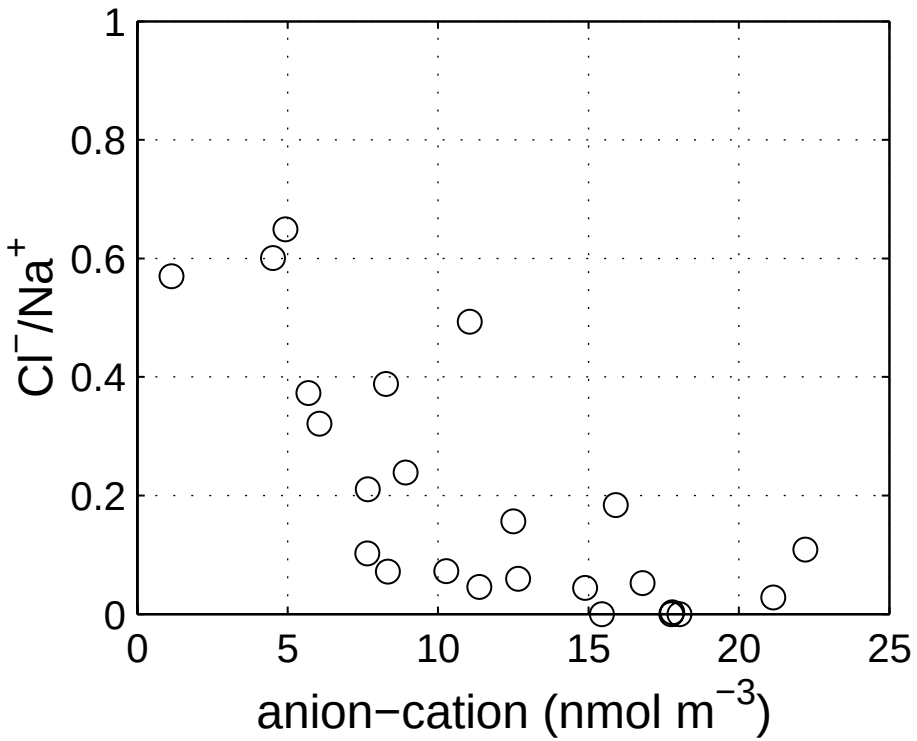

Fig. 8. The fpm Cl^-/Na^+ molar ratio as a function of the difference between the analysed cations and anions (referred to as acidity) for samples in the IInd and sInd trajectory groups during the Ronald H. Brown cruise in 1999.

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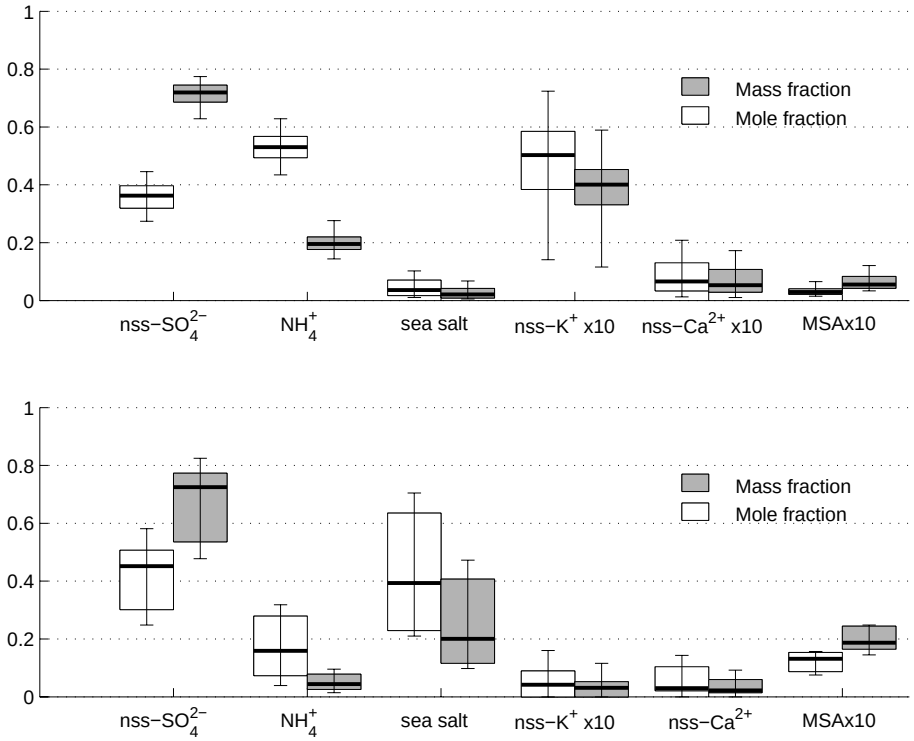

Fig. 9. The median molar and mass fractions (thick horizontal line) of the analysed components for the Ronald H. Brown 1999 cruise, **(a)** north of the ITCZ, median 3.2 μg m^{-3} total analysed mass, **(b)** south of the ITCZ, median 0.5 μg m^{-3} total analysed mass. The box includes data between the 25 and 75 percentiles and the vertical bars represent the 10 and 90 percentiles.

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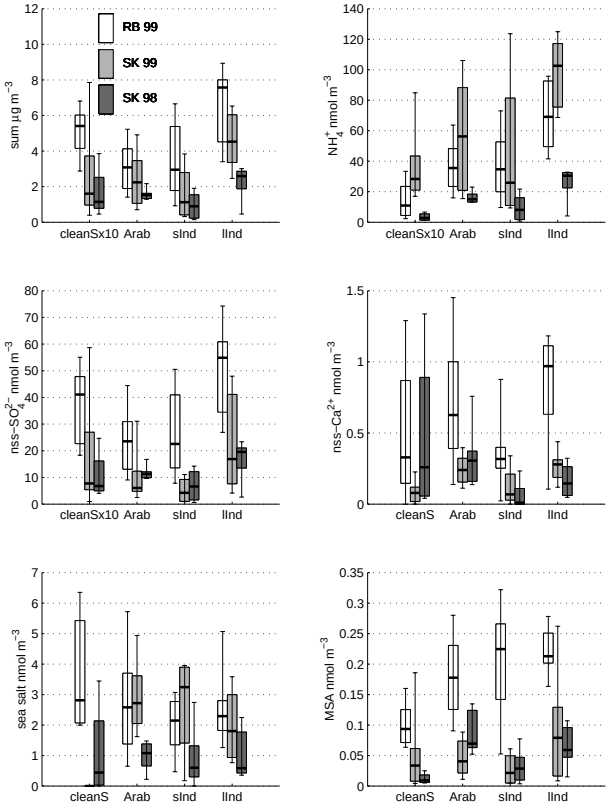

Fig. 10. The median concentrations (thick horizontal line) for the three cruises divided into different trajectory groups. **(a)** fpm sum, **(b)** NH_4^+, **(c)** nss-SO_4^{2-}, **(d)** nss-Ca^{2+}, **(e)** sum of the sea salt components, **(f)** MSA. The box includes data between the 25 and 75 percentiles and the vertical bars represent the 10 and 90 percentiles.

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